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Influence of silanes on the shear bond strength of resin cements to zirconia

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Influence of silanes on the shear bond strength of resin cements to zirconia

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Zirconia, silanes, universal silane, self-adhesive resin cement, resin cements, shear bond strength, pre-treatment, aging

Abstract

Objectives: To test the shear bond strength of self-adhesive and conventional resin cements to zirconia after the application of different types of silanes with/without aging.

Methods: Threehundred-and-sixty zirconia specimens were radomised into 10 groups (n=36). Five groups were assigned to the self-adhesive-resin-cement RelyX-Unicem(RXU) and 5 groups to the conventional-resin-cement Panavia21(PAN). The groups were further assigned to the following pre-treatments: I)Monobond-S (M), II)Alloy Primer (AP), III)Clearfil (C), IV)Experimental-Universal-Primer(EUP), V)without-silane (control group). Twelve specimens each of the cements were tested after water-storage for 24 hours (initial shear bond strength). The remaining 24 samples were aged (1500 cycles,n=12/13500 cycles,n=12). The shear bond strength was measured (Universal-Testing-Machine;1mm/min, Zwick Z010). Data were analysed with one-way ANOVA followed by post-hoc Scheffé tests. Student`s t-test was applied to test the differences between the two cements ($p<0.05$).

Results: The initial bond strength of RXU was increased by the application of the different silanes. The silanes had less influence on the initial bond strength of PAN. Aging reduced the bond strength of RXU significantly in combination with two of the silanes (AP: 0±0 MPa; C: 4.1± 0.9MPa; $p<0.05$). Aging led to a significant reduction of the bond strength values at PAN at the primers AP (2.9±0.4MPa) and EUP (2.5± 0.5MPa; 0<0.05).

Conclusion: The present study indicated that the bond strength of the self-adhesive resin cement was positively influenced by the pre-treatment of the zirconia surface with different silanes. Aging led to a decrease of the bond strength at both types of cements, irrespective of most of the silanes.

Introduction

The high-strength ceramic zirconia exhibits promising clinical performance as framework material for all-ceramic crowns and fixed dental prostheses (FDPs)[1,2]. Very few fractures of zirconia frameworks were reported until today[1,2]. These good results were associated with the excellent mechanical and physical properties of zirconia when compared to other ceramics[3,4].

Zirconia is a polycrystalline high-strength ceramic which does not contain a silica glass matrix. Due to its specific chemical composition the adhesive cementation of zirconia can only be accomplished with specific resin cements[5,6,7].

Zirconia cannot be roughened by hydrofluoric acid etching used for the pre-treatment of glass-ceramics[8,9]. Additionally, the conventional silanes used for glass-ceramics do not chemically bond to zirconia. These silanes improve the bond strength between the ceramic and the resin cement by forming a siloxane cross linking with the silica in the glass-ceramic[9]. Since zirconia is free of silica different types of silanes and resin cements are needed as for glass-ceramics[5,14]. The clinical procedures associated with the cementation of zirconia-based reconstructions can be complicated due to the fact, that clinicians need to be aware of the chemical composition of zirconia and the suitable resin cements for its adhesive cementation. Recently, a number of different resin cements and new silanes were introduced to improve the adhesive fixation of zirconia- based reconstructions.

In order to provide chemical bonding to zirconia the silanes and/or resin cements need to contain acidic monomers like e.g. phosphate monomer 10- methacryloyloxydecyl dihydrogen phosphate (MDP)[5,6,7,10]. Recent studies showed that resin cements with acidic monomers led to significantly higher bond strength values compared to conventional resin cements without acidic monomers [4,5,6,7,9,10]. Furthermore, the application of a MDP- containing silanes (e.g. Clearfil New Bond and Clearfil Porcelain Bond Activator) significantly increased the shear bond strength of resin cements (e.g. Panavia 21) to zirconia[11].

Due to the fact that resin cements are hydrophobic numerous pre-treatment priming and bonding steps are needed for the chemical bonding to dentin. As a consequence, the adhesive cementation is a very technique sensitive procedure in the clinical practice. Clinical problems like the contamination[28] of the surface with saliva or blood[15], or errors at the application of the pre-treatment solutions or the cements[16] lead to a significant decrease of the bond strength values. In addition, the chemical compatibility of the resin cements and the different restorative materials needs to be considered, as indicated above.

Recently developed self-adhesive resin cements aim for a simplification of the adhesive cementation. These resin cements bond to both tooth substance and different materials without a specific pre-treatment[17]. Self-adhesive resin cements with acidic monomers like e.g. RelyX Unicem (ESPE, Germany) exhibited promising results in laboratory and clinical studies[17]. Interestingly, good bonding performance of this cement was observed at zirconia[12,13]. It has been demonstrated that the initial bond strength of resin cements generally is reduced by aging in the humid oral environment. Yet, the application of silanes led to a stabilisation of the bond strength values and, hence, to less influence of aging[4].

In order to simplify the silanisation, universal silanes which chemically bond to different types of materials were recently introduced. These universal silanes and/ or resin cements could significantly simplify the clinical procedures at the cementation of zirconia- based reconstructions and would be very desirable out of a clinical perspective, provided that the materials are compatible. No studies of the influence of these silanes, or their interaction with different types of resin cements and materials are available until today.

The aim of this study, therefore, was to test whether or not the shear bond strength of conventional and self-adhesive resin cements to zirconia is influenced by the application of the different types of silanes. Furthermore, the effect of the silanes on the bonding performance of the cements at ageing was analysed.

The following hypotheses were tested: (1) the shear bond strength of self-adhesive and conventional resin cements to zirconia is improved by the application of conventional and/or universal silanes, (2) the shear bond strength of the two types of cements is less prone to ageing through the application of the respective silanes.

Material and Methods

The shear bond strength of two resin cements, one self- adhesive resin cement (RXU: RelyX Unicem, 3M ESPE , Seefeld, Germany) and one conventional resin cement (PAN: Panavia 21, Kuraray Europe GmbH, Frankfurt a.M., Germany) to zirconia was tested in combination with the application of the following silanes and primers, respectively:

One methacrylate-acid-containing silane (M: Monobond S, Ivoclar Vivadent, Schaan, Liechtenstein), 2 phosphate-monomer-containing silanes (C: Clearfil Porcelain Bond Activator, Kuraray Europe GmbH, Frankfurt a.M., Germany; AP: Alloy Primer, Kuraray Europe GmbH, Frankfurt a.M., Germany) and one universal silane (EUP: Experimental Universal Primer*, Ivoclar Vivadent, Schaan, Liechtenstein)

The detailed information on the chemical composition, lot numbers and brands of the silanes and primers is given in Table 1.

Specimen preparation

Densely sintered zirconia blanks (Cercon, DeguDent, Hanau, Germany) were used for the fabrication of the zirconia specimens. The blanks were cut into 360 disk shaped specimens with a diameter of 20 mm and a thickness of 2 mm. The specimens were embedded in acrylic resin, exposing the top surface of the ceramic. The exposed zirconia surface of specimens was polished to high gloss (Abramin, Struers, Denmark).

The 360 polished zirconia specimens were divided into 10 groups of 36 specimens each.

5 of these groups were assigned to the self-adhesive resin cement RelyX Unicem (RXU).

The remaining 5 groups were assigned to the conventional resin cement Panavia 21 (PAN).

For both cements the groups were further assigned to the following pre- treatment methods (test). For both resin cements, no treated specimens acted as control groups:

* EUP was a prototype silane, it was a first version of the further developed and now available silane Monobond Plus (Ivoclar Vivadent). At time of the study EUP was not approved for the clinical application.

RXU:	test	● RelyX Unicem- Monobond S	(RXU- M	n=36)
		● RelyX Unicem- Alloy Primer	(RXU- AP	n=36)
		● RelyX Unicem- Clearfil	(RXU- C	n=36)
		● RelyX Unicem- Experimental Universal Primer	(RXU- EUP	n=36)
	control	● RelyX Unicem- no silane/primer	(RXU	n=36)
PAN:	test	● Panavia 21- Monobond S	(PAN- M	n=36)
		● Panavia 21- Alloy Primer	(PAN- AP	n=36)
		● Panavia 21- Clearfil	(PAN- C	n=36)
		● Panavia 21- EUP	(PAN- EUP	n=36)
	control	● Panavia 21- no silane/primer	(PAN	n=36)

The zirconia surface of the specimens was cleaned with alcohol. Subsequently, the specimens were pre-treated with the respective silanes following the manufacturers' instructions (Table 2) and the resin cements were applied to the pre-treated surfaces. The specimens of the control groups were cleaned and the resin cements were directly applied to the non-treated surfaces.

The specimens were mounted in a customized holding device (Fig.1) with the exposed zirconia surface on the top. For the standardized application of the resin cements acrylic cylinders with an inner diameter of 2.9mm (D+R Tec, Birmensdorf, Switzerland) were mounted on the zirconia surface by means of the holding device, thus defining the bonding area for the resin cements at 6.605 mm^2. The procedures used for the standardized application of the resin cements and the shear bond strength test were published in detail elsewhere[18] and will only be briefly summarized.

The cements were applied into the cylinders according to the manufacturers' recommendations (Table 2), and a steel screw (inner hexagon, outer diameter of 2.8 mm) was inserted into the cylinder applying a standardized load on the cements of 100 g (Fig.2).

With this procedure the thickness of the resin cement layers was set at 0.5 mm for all specimens. The excess resin cement was carefully removed with pallets.

All specimens cemented with RXU (n=36) were light cured with LED polymerization lamp (Elipar Freelight 2: 3M ESPE; Seefeld, Germany) for 20 seconds as recommended by the manufacturers. The 36 PAN specimens were allowed for chemical curing for 10 minutes at 37°C. After the setting of the cements the specimens were stored in distilled water (37°C) for 24 hours.

Twelve samples each of the cements were tested straight after the storage in water (initial shear bond strength). The remaining 24 samples of each cement were aged by means of thermocycling (Thermocycler, Willitec, Gräfeling, Germany). Twelve specimens of each group were aged with 1500 thermal cycles (5° and 55° C, 30-s dwell time). The remaining specimens (n=12) were tested after 13500 thermal cycles.

Shear bond strength test

The shear bond strength test was carried out in an universal testing machine (Zwick/Roell Z010, Ulm, Germany) with load applied at a cross head speed of 1 mm/min. For this, the specimens were positioned by means of a special sample device (Fig.3) with the zirconia surface parallel to the loading piston and the chisel of the loading piston was adjusted. The load was applied to the cylinder with a 300 µm distance of the piston to the surface of the specimen. The load at debonding of the cylinders was recorded in Newtons (N). For further analysis the load values were converted to MPa by dividing the failure load (N) by the bonding area (mm^2).

Statistical Analysis

The statistical analysis was made using Statistical Package for the Social Science Version 19 (SPSS INC, Chicago, IL, USA). Descriptive statistics were computed. Within each pre-treatment and aging group differences between mean shear bond strength values of the groups were analyzed by one-way ANOVA, followed by a post-hoc Scheffé test. Additionally, Student's t-test was applied to test the differences between the two resin cements. P-values smaller than 5% were considered to be statistically significant in all tests.

Results

Detailed information on the respective shear bond strength values of the groups with and without application of silanes and the differences between groups are given in Table 3.

Influence of the application of silanes on the shear bond strength (TC=0)

At all-time points the application of the silanes increased the shear bond strength of the self-adhesive resin cement RXU as compared to the samples without any pre-treatment. In contrast, the application of most of the silanes did not have an influence on the bond strength of the conventional cement PAN. At this resin cement solely the silane C had a positive effect. (Table 3)

Influence of the aging (1500TC, 13500TC)

Aging had a significant influence on the bond strength of RXU at the zirconia samples that were pre-treated with C and AP. A significant reduction of the bond strength values was observed at these samples. No reduction of the bond strength was found at the samples pre-treated with the other silanes and at the specimens without pre-treatment (Fig. 4).
Ageing had a significant influence also on the conventional resin cement PAN. In general, the bond strength was reduced after the aging (Fig. 5). At the samples pre-treated with AP, C and EUP the decrease was significant as compared to the initial bond strength. (Table 3)

Comparison of the shear bond strength of the two cements

No significant difference of the initial shear bond strength values was found when the conventional cement PAN and the self-adhesive resin cement RXU were compared. Furthermore, aging did not exhibit a pronounced influence on the comparison of the two resin cements. Only in two of the tests a statistically significant difference between PAN and RXU was found (Table 4).

Discussion

The first part of this study tested the effect of different silanes on the shear bond strength of the self-adhesive resin cement RXU and the conventional resin cement PAN to zirconia. The shear bond strength of RXU was increased by the application of the silanes. In contrast, the application of most of the silanes did not have any influence on the conventional resin cement PAN. Hence, the first hypothesis could only be accepted for the self-adhesive resin cement RXU.

The second part of this study investigated the influence of aging on the shear bond strength of RXU and PAN after pre-treatment of zirconia with the respective silanes. Aging had a highly varying influence on the bond strength of the tested silanes and cements. At RXU aging reduced the bond strength significantly in combination with two of the silanes (AP, C). No influence, however, was found at the specimens without silane pre-treatment or at the specimens pre-treated with M and EUP. At PAN a significant reduction of the bond strength was observed in combination with the silanes AP and EUP after the ageing. Aging, however, had no influence on the specimens treated with the other pre-treatment methods. Thus, the second hypothesis was rejected.

The results of the present study are of significance for the everyday clinical practice. They indicate, that the newly developed universal resin cements and silanes are not necessarily compatible with conventionally used adhesive materials, and in contrast to improving the bonding quality, can even lead to a reduction of the bond strength if combined inappropriately. It is, therefore, of high importance for good long-term stability of the bonding, that only specific combinations are used at the adhesive cementation.

In the present study pre-treatment with MDP containing silanes or primers (C, AP) increased the shear bond strength between the zirconia and the self-adhesive resin cement RXU. The increase of the shear bond strength was also shown in a study by De Souza et al[20]. Kern et al[32] indicated that this increase most likely is caused by a chemical interaction between MDP and zirconia. This assumption is supported by the results of several studies. The phosphate ester monomer of MDP was shown to bond directly to the oxides of alumina and zirconia[32,33,37] . This chemical interaction also lead to higher shear bond strength of MDP containing resin cements to zirconia[4,9,13,17,23,35,38,39]. Blatz et al[4] showed that the phosphate ester monomer of MDP exhibited a positive influence irrespective of the fact whether the monomer was part of the silane or of the resin cement.

In most of the studies[9,30,36,37] the silane C increased the shear bond strength between PAN and zirconia. This finding was not supported by the results of the present study, though. The differences of the results might be caused by the different study protocols. In the present study no air-particle abrasion of the zirconia was performed, while in other investigations the zirconia surface was roughened by air-particle abrasion[21]. Numerous studies showed to that air-particle abrasion positively influenced the shear bond strength between resin cement and zirconia[,21,23,29,34]. Future studies are needed to test the influence of a combination of air-particle abrasion and application of silanes on the bond strength of resin cements to zirconia.

Aging had a negative influence on the shear bond strength of both types of resin cements to the zirconia. This observation is supported by numerous studies [6,7,11,13,14]. In contrast, Lindgren et al[22] reported no significant influence of aging on the shear bond strength of RelyX Unicem with the metal primer. In this study aging was performed by means of storage in water and/or thermocycling. The most values of the shear bond strength decreased salient after 1500 thermocycles as also after 13500 thermocycles.

The experimental universal silane EUP that was tested in the present study had no influence on the shear bond strength values compared to the other silanes in the present study. This result was discouraging and clearly indicated that this prototype silane needed significant further improvement prior to the introduction to the clinical practice. Furthermore, studies of the ready developed version of the protoype EUP are needed to confirm its application in the presently tested combinations for the adhesive fixation of zirconia- based reconstructions.

One of the reasons for the differences of the results of the present and other studies might be the different testing procedure. In a recent review of the literature by Heintze et al[25,26,27] the different in-vitro testing procedures were compared. In most of the shear bond strength tests composite cylinders were bonded to flat polished surfaces and the shear bond strength test was performed with a specific testing machine. The author concluded that the shear bond strength test was easy and fast, however, the results were highly influenced by the operator or specific settings of the testing machines. Factors such as the positioning of the shearing blade on the specimens or high forces applied by the blade exhibited a high influence on the bond strength values. Furthermore, the way the specimens were aged, i.e. whether or not thermocycling was performed, had a significant impact on the bond strength values. The review showed that in most of the studies solely storage in water for 24h was used as aging. The authors concluded that for the analysis of the long-term bond strength of silanes and/or resin cements to various materials aging for a minimum of 3 months should be performed[42] . Hence, in the present as well as in other studies the simulation of the oral conditions by means of thermocycling had an important effect on the durability of the resin bond strength to zirconia and might be the reason for the differences of the results [4,5,31,35].

Conclusion

In conclusion, the present study indicated that the shear bond strength is affected by the pre-treatment of the zirconia surface with different silanes. This finding is of specific interest for the daily clinical practice, since new simplified resin cements and adhesive agents (like e.g. silanes) are constantly being introduced in order to improve the bonding to zirconia. Hence, clinicians need to take care of the chemical compatibility of the components used. Interestingly, in the present study no difference was found between the self-adhesive and the conventional resin cements. This indicates, that even with simplified adhesive luting procedures using self-adhesive resin cements good bond strength to zirconia can be achieved. The additional application of compatible silanes increases the bonding capacity of the self-adhesive cement.

Yet, since the presently applied shear bond strength test is critical out of the above mentioned reasons, studies using more standardized procedures like the microtensile test[40,41] should be performed to test the present observations in more detail.

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6. References

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7. Tables and Figures

Table 1 Summary of products used.

Group	**Cement**	**Company**	**LOT-Nr**
RXU	RelyX Unicem	3M ESPE , Seefeld, Germany	300136/290546/287407
PAN	Panavia 21	Kuraray Europe GmbH, Frankfurt a.M., Germany	00406C UNI TC/ 00647C CAT
Group	**Adhesive**	**Company**	**LOT-Nr**
M	Monobond S	Ivoclar Vivadent, Schaan, Liechtenstein	J23960
AP	Alloy Primer	Kuraray Europe GmbH, Frankfurt a.M., Germany	239AA
C	Clearfil porcelain Bond Activator	Kuraray Europe GmbH, Frankfurt a.M., Germany	00201B/Primer:00653A
EUP	Experimental Universal Primer	Ivoclar Vivadent, Schaan, Liechtenstein	R38-082-2

Table 2 Detailed information on the application of the resin cements and silanes.

Name	Application steps
RelyX Unicem (RXU)	Activation of Aplicap capsule in the Aplicap Activator (3M ESPE, Seefeld, D) for 2- 4 s. Mixing of the capsule for 10 s in the RotoMix (3M ESPE, Seefeld, D) Application of cement to the substrate surface with the Aplicap Applier (3M ESPE, Seefeld, D).
Panavia 21 (PAN)	Mix the catalyst and universal pastes for 20-30 seconds, creating a homogenous paste. Application of cement to the substrate with a spatula. Application of Oxyguard II to all margins for 3 min remove by rinsing with water
Monobond S (M)	Application the liquid with a brush. 1 minute to influence leave and and dry with a gentle airflow
Alloy Primer (AP)	Apply a thin layer on the surface. 5 seconds to influence leave
Clearfil Porcelain Bond Activator (C)	Clearfil SE Primer and Clearfil Porcelain activator are mixed with one another 1:1. Application the liquid on the surface. Leave for 20s. Blow the solvents with a gentle airflow.
Experimental Universal Primer (EUP)	Apply a thin layer with a brush and leave influence 60 seconds. Blow with air thoroughly

Table 3 Results: p- value, mean difference (Mean) and 95% CI

ANOVA Influence of aging within a pretreatment: A/B

ANOVA Influence of the primer at one time: a/b

Values labeled with A(a) are statisticaly different from the ones labeled with B(b)

Values labeled with AB(ab) do not differ from the ones with A(a) or B(b)

RXU		-	M	AP	C	EUP
0 TC	p, (Mean)	$1.4(0.7)_{A}^{a}$	$5.3(0.9)_{A}^{ab}$	$5.2(0.8)_{B}^{ab}$	$8.1(1.1)_{B}^{b}$	$4.7(0.8)_{A}^{ab}$
	95% CI	(-0.2;3.1)	(3.2;7.4)	(3.4;7.0)	(5.7;10.6)	(2.9;6.6)
1500 TC	p, (Mean)	$2.6(0.7)_{A}^{a}$	$3.2(0.9)_{A}^{a}$	$4.1(1.1)_{B}^{ab}$	$7.7(0.5)_{B}^{b}$	$3.9(0.7)_{A}^{a}$
	95% CI	(1.1;4.2)	(1.2;5.3)	(1.7;6.6)	(6.5;8.9)	(2.3;5.6)
13500 TC	p, (Mean)	$2.4(0.7)_{A}^{ab}$	$5.3(1.4)_{A}^{b}$	$0(0)_{A}^{a}$	$4.1(0.9)_{A}^{ab}$	$5.3(1.4)_{A}^{b}$
	95% CI	(0.8;4.0)	(2.1;8.4)	(0;0)	(2.1;6.1)	(2.1;8.6)
PAN		-	M	AP	C	EUP
0 TC	p, (Mean)	$4.0(0.4)_{A}^{a}$	$4.2(0.4)_{A}^{ab}$	$5.0(0.5)_{B}^{ab}$	$6.0(0.5)_{B}^{b}$	$5.4(0.3)_{B}^{ab}$
	95% CI	(3.0;4.9)	(3.4;5.1)	(3.9;6.0)	(4.9;7.1)	(4.8;6.1)
1500 TC	p, (Mean)	$7.5(1.0)_{B}^{b}$	$4.8(0.3)_{A}^{a}$	$5.3(0.4)_{B}^{ab}$	$4.2(0.3)_{A}^{a}$	$4.0(0.6)_{AB}^{a}$
	95% CI	(5.2;9.9)	(4.2;5.4)	(4.3;6.3)	(3.5;4.9)	(2.7;5.4)
13500 TC	p, (Mean)	$3.3(0.6)_{A}^{a}$	$3.9(0.4)_{A}^{a}$	$2.9(0.4)_{A}^{a}$	$3.2(0.4)_{A}^{a}$	$2.5(0.5)_{A}^{a}$
	95% CI	(1.9;4.6)	(3.0;4.8)	(1.3;3.3)	(2.2;4.2)	(1.4;3.5)

Table 4 Results: p- value, mean difference (Mean) and 95% CI

RXU vs. PAN		-	M	AP	C	EUP
0 TC	p, (Mean)	0.005	0.315	0.832	0.780	0.418
	95% CI	(-4.26; -0.83)	(-1.09; 3.17)	(-1.69; 2.09)	(-0.26; 4.62)	(-2.59; 1.14)
1500 TC	p, (Mean)	0.001	0.123	0.332	<0.001	0.945
	95% CI	(-7.48; -2.34)	(-3.59; 0.48)	(-3.71; 1.33)	(2.20;4.74)	(-2.02; 1.89)
13500 TC	p, (Mean)	0.349	0.360	<0.001	0.371	0.080
	95% CI	(-2.83; 1.04)	(-1.77; 4.54)	(-3.23; -1.35)	(-1.13; 2.97)	(-0.39; 6.15)

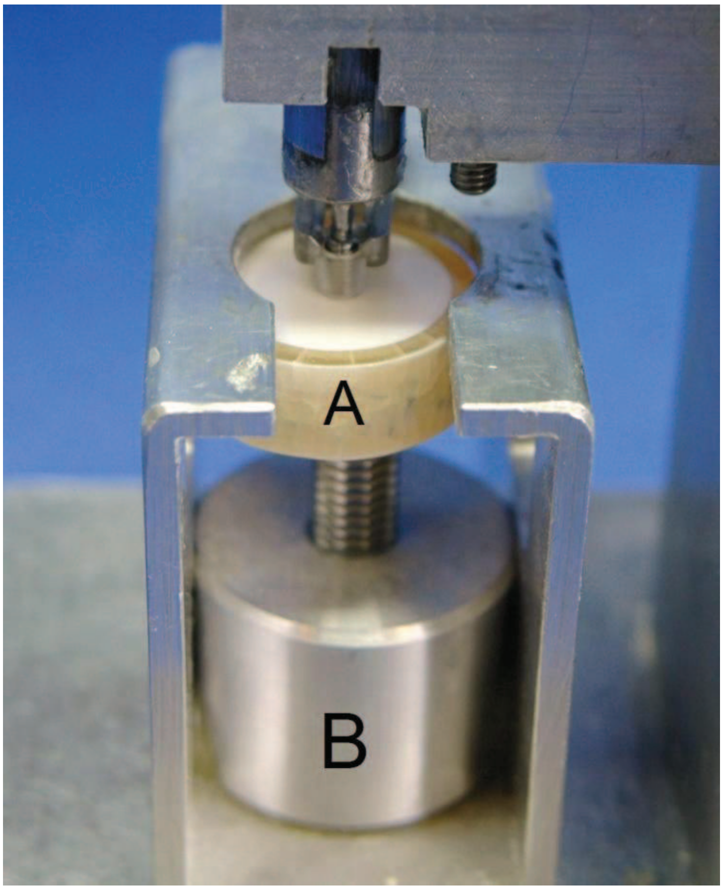

Figure 1

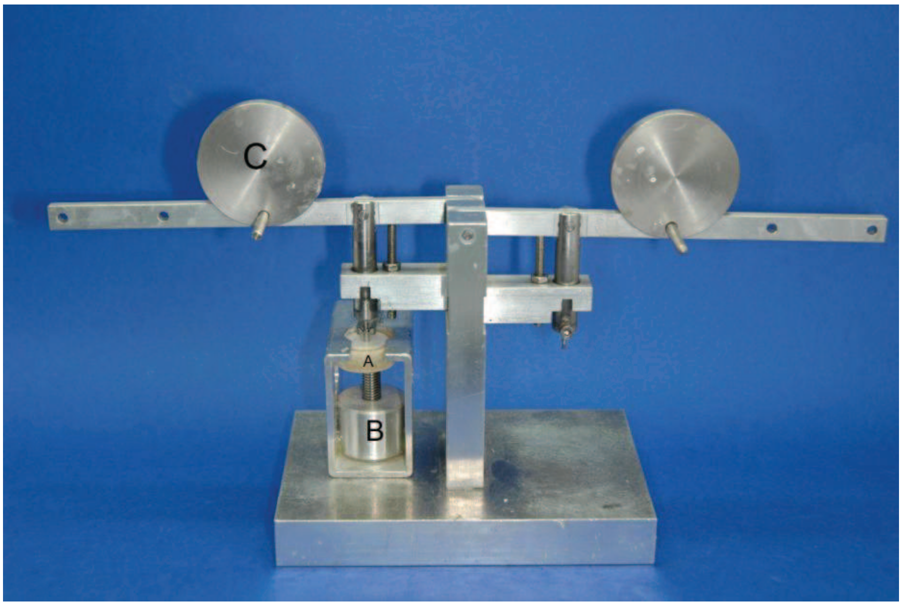

Figure 2

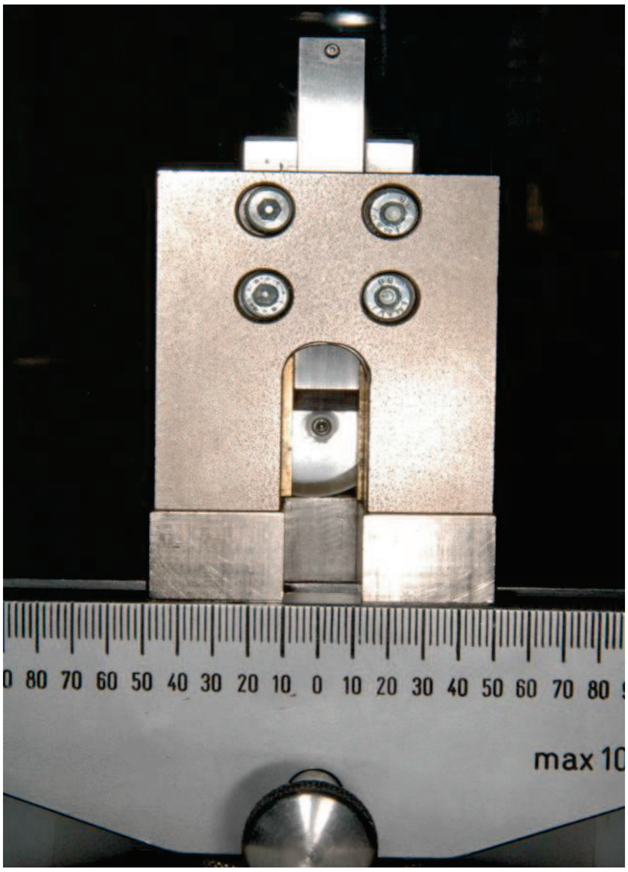

Figure 3

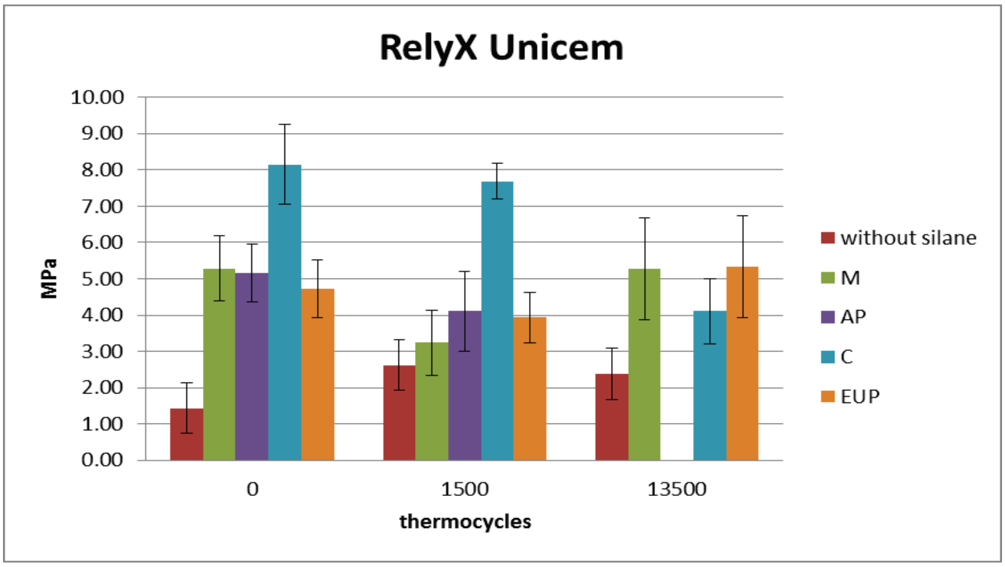

Figure 4

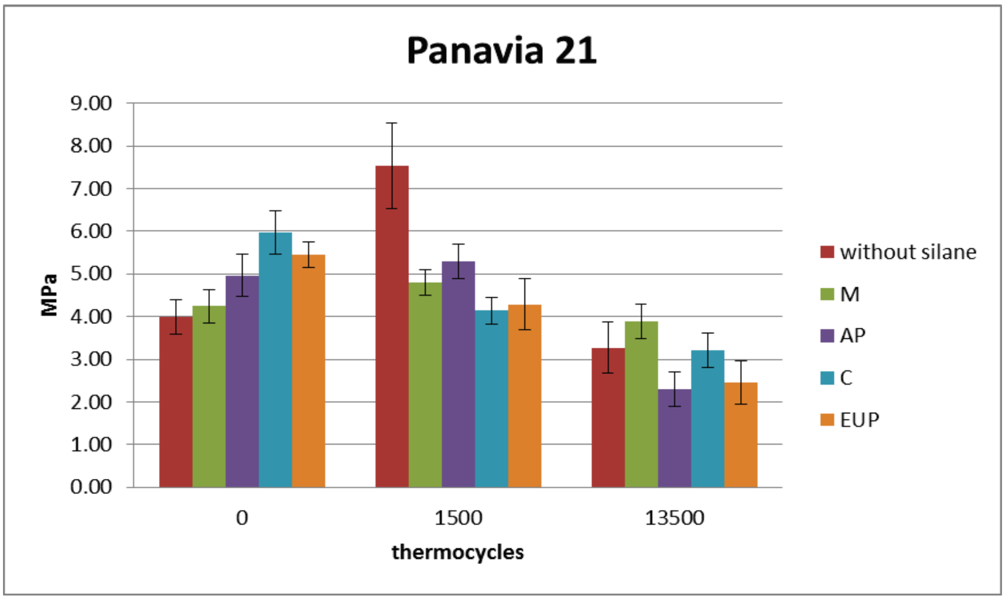

Figure 5

Figure legends:

Figure 1 Bonding device. A= fixed specimen, B= holder.

Figure 2 Bonding device. A= fixed specimen, B= holder,
C= load simulating finger pressure (100g).

Figure 3 Test device of shear bond strength.

Figure 4 Mean values and standard deviations of the shear bond strength in MPa of the self-adhesive resin cement RelyX Unicem with the different pre-treatments and the aging (0TC, 1500TC, 13500TC).

Figure 5 Mean values and standard deviations of the shear bond strength in MPa of the conventional resin cement Panavia 21with the different pre-treatments and the aging (0TC, 1500TC, 13500TC).

Curriculum Vitae

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• **Klinisches Studium der Zahnmedizin** an der Universität Zürich	2004- 2007
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• **Studium der Zahnmedizin** an der Universität Zürich	2001-2004
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